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Hazardous compounds in recreational and urban recycled surfaces made from crumb rubber. Compliance with current regulation and future perspectives

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HIGHLIGHTS

- 40 recycled rubber recreational and urban pavements (indoor/outdoor) were analyzed.
- 42 chemicals including suspected carcinogens and endocrine disruptors were considered.
- Sum of PAH concentrations at parts per million were found in all rubber surfaces.
- Most samples fulfill the new EU regulation but exceed PAH limit in consumer products.
- Green materials were free of hazardous compounds, then offering a safe alternative.

GRAPHICAL ABSTRACT

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ABSTRACT

Crumb rubber obtained from scrap tires is greatly employed for the construction of different facilities for sport, recreational and other uses. However, in recent years the concern about their safety and the related adult and children exposure to these surfaces is growing. This study aims a thorough chemical characterization encompassing 42 hazardous compounds, including polycyclic aromatic hydrocarbons (PAHs), phthalates, adipates, antioxidants and vulcanization agents in a wide range of crumb rubber from different surfaces. For the extraction of the target compounds, a method based on ultrasound-assisted extraction followed by gas chromatography-tandem mass spectrometry (UAE-GC–MS/MS) has been validated. Forty crumb rubber samples coming from synthetic turf football pitches, outdoor and indoor playgrounds, urban pavements, commercial tiles and granulates, and scrap tires, were analyzed. In addition, green alternative materials, such as sand and artificial turf based on cork granulate infill were included to compare the levels of the target compounds with those of crumb rubber. Most of the analyzed recycled surfaces meet the recent limits proposed by the European Commission for rubber granulates and mulches, although they exceed in several cases the maximum levels allowed for rubber consumer products. Besides, most of the other target compounds, including several of them considered as endocrine disruptors, were detected in the analyzed samples, reaching parts per million concentrations.

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1. Introduction

The European Union (EU) is the second largest generator of scrap tires after United States, and according to the EU landfill and the end-of-life (EOL) vehicles directives, the national governments are obliged to address its recycling for safety, health and environmental purposes (Directive 2000/76/EC, Directive 2000/53/EC, Sebola et al., 2018).

The different processes and strategies proposed for the recycling of scrap (end-of-life) tires involve, among others, pyrolysis, controlled incineration, or mechanical crushing, the last one being the most employed one for its simplicity and low-cost. The obtained crumb rubber can be used in two different ways. Firstly, as infill in roads or sport surfaces such as artificial turf facilities (Janes et al., 2018), either as bound forms employed for the construction of tiles widely used in both outdoor and indoor safe surfaces such as playgrounds, schoolyards, nurseries, gym floors, and in urban pavements like walkways, tree protection or street furniture. However, several scientific studies have revealed the presence of hazardous compounds in the crumb rubber employed for the manufacture of recycled recreational surfaces. The presence of heavy metals has been reported (Bocca et al., 2009; Janes et al., 2018; Menichini et al., 2011), especially Cr, Cu, Ni, Pb and Zn at hundreds and even thousands of $\mu g\ g^{-1}$, then, exceeding the limits established by some regulations regarding the maximum concentration allowed in soils (Bocca et al., 2009). The presence of a high number of organic compounds, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), paraffins, benzothiazoles, plasticizers, antioxidants, or phenols, among others have been also reported in the crumb rubber employed for playgrounds and synthetic turf pitches (Brandsma et al., 2019; Celeiro et al., 2014; Diekmann et al., 2019; Llompart et al., 2013; Schneider et al., 2020b). The presence of most of these hazardous compounds is expected in this recycled material, since most of the recycled rubber stems from shredded end-of-life tires, the main components of which are rubber polymers (up to 60%) and aromatic extender oils (up to 30%). Besides, the called 'carbon black', used as a reinforcing filler, is estimated to make up to 20 to 30% of every tire, and contains antioxidants, antiozonants and vulcanization agents (Diekmann et al., 2019).

The European Union (EU) applicable regulation for the crumb rubber is confusing, whereas the concern about the safety of this recycled material is increasing. As for the eight PAHs considered as carcinogenic by the ECHA (European Chemicals Agency): Benzo[*a*]pyrene (B[*a*]P), dibenzo[*ah*]anthracene (D[*ah*]A), benzo[*e*]pyrene (B[*e*]P), benzo[*a*]anthracene (B[*a*]A), chrysene (CHY), benzo[*b*]fluoranthene (B[*b*]F), benzo[*j*]fluoranthene (B[*j*]F), and benzo[*k*]fluoranthene (B[*k*]F) the European Commission restricts their contents to 1 $\mu g\ g^{-1}$ in consumer goods and to 0.5 $\mu g\ g^{-1}$ in materials 'with intensive contact' such as toys (JRC, 2018, Off. J. Eur. Union, 2013). Until now, the crumb rubber has been considered as a mixture. The concentration limits for PAHs in mixtures supplied to the general public have been set at 100 $\mu g\ g^{-1}$ for B[*a*]P, and D[*ah*]A, and up to 1000 $\mu g\ g^{-1}$ for other 6 PAHs (B[*e*]P, B[*a*]A, CHY, B[*b*]F, B[*j*]F and B[*k*]F). Recently, the EU proposed the restriction of PAHs in granules and mulches used in synthetic turf pitches and playgrounds (EC, 2018). This restriction intends to ensure that the cancer risk from exposure to the chemicals remains at a low level for those coming into contact, via inhalation and skin contact, with the crumb rubber. Several European countries such as Netherlands, by the Dutch National Institute for Public Health and the Environment (RIVM), suggested a combined concentration limit of 17 $\mu g\ g^{-1}$ for the eight ECHA PAHs (ECHA, 2018) in these materials. On September 2019, based on this proposal and on the earlier opinion expressed by the Committee for Risk Assessment (RAC), the Committee for Socio-Economic Analysis (SEAC) adopted its final opinion: the restriction of the eight ECHA PAH total concentration to 20 $\mu g\ g^{-1}$ in the granules and mulches used in synthetic turf pitches and playgrounds (ECHA, 2019). Now, following the SEAC's final opinion, the European Commission will prepare a draft restriction measure to amend the REACH Restrictions list (EC, 2018) prior its entry into force (REACH, 2020).

In the United States, the Environmental Protection Agency (US EPA) and other agencies are also conducting studies to assess the potential human exposure of PAHs from tire crumb rubber employed as infill in synthetic turf sport facilities (EPA, 2016). A study dealing with the identification of chemical compounds, and the human exposure to this material, has been recently published (EPA, 2019). The study suggests exploring the feasibility of in-vitro studies to assess bioaccessibility and cytotoxicity, as well as in-vivo studies to evaluate the short-term toxicity effects from different exposure routes.

The primary route of human exposure is by dermal contact and oral intake (Diekmann et al., 2019), and recent studies suggest that the risk of cancer for children is 10 times higher if exposed to rubber surfaced playgrounds in comparison with uncovered surfaces (Tarafdar et al., 2019). In addition, the exposure of outdoor crumb rubber surfaces to different meteorological conditions favours the volatilization of these compounds which could be easily inhaled (Celeiro et al., 2018; Celeiro et al., 2014; Schneider et al., 2020a), or dragged by runoff water before reaching the sewage systems (urban pavements), or environmental waters (rubber recycled facilities close to rivers or lakes) (Celeiro et al., 2018, 2014; Diekmann et al., 2019). On the other hand, in last years, several green alternatives based on the use of cork or coconut crumb, are gaining interest to substitute the rubber infill, and several hybrid-natural sport surfaces are being tested with promising features.

Different extraction techniques have been reported for the analysis of PAHs, antioxidants or phenols in the crumb rubber (Li et al., 2010; Marsili et al., 2015). However, most of these techniques require several time-consuming steps and a high volume of organic solvents. A suitable option is the use of ultrasound-assisted extraction (UAE), a fast and reliable technique, followed by gas chromatography-tandem mass spectrometry (GC–MS/MS), which offers both a high sensitivity and selectivity to determine trace levels of the target compounds.

Therefore, this work aims at evaluating the presence of 42 hazardous compounds including 18 PAHs, 19 plasticizers (phthalates, adipates, and bisphenol A), 2 antioxidants and 3 acceleration and anti-degradants agents, in crumb rubber samples. Forty samples, including those collected from football pitches of synthetic turf and playgrounds, were considered. Besides, commercial tiles and crumb rubber, and urban pavers were analyzed to obtain a thorough characterization of a wide range of different rubber recycled surfaces, as well as car tires. In addition, a comparison between the crumb rubber and alternative green materials, such as cork crumb and sand, was performed.

2. Experimental

2.1. Reagents and materials

The studied compounds and their CAS numbers are summarized in Table S1. Ethyl acetate (EtAc) was provided by Sigma-Aldrich (Steinheim, Germany), methanol (MeOH) was supplied by Scharlab (Barcelona, Spain), and acetone was provided by Fluka Analytical (Steinheim, Germany).

Individual stock solutions of each compound were prepared in methanol or ethyl acetate. Further dilutions and mixtures were prepared in acetone (spike solutions) or ethyl acetate (calibration studies). Stock solutions were stored in glass vials protected from light at −20 °C. All reagents were of analytical grade.

2.2. Sampling procedure

Forty samples from outdoor and indoor recreational surfaces, urban pavements, commercial rubber tiles, and car tires were analyzed. Besides, two alternative materials were included in this study. Details about the analyzed samples are given in Table S2.

The crumb rubber samples were directly collected from the studied surfaces in the region of Galicia (Northwest Spain). A similar number of crumb rubber samples from football pitches (13) and playgrounds (15) were collected. In the case of playgrounds, 10 were taken from outdoor playgrounds and 5 samples from indoor playing areas, since the number of indoor playgrounds is lower than the outdoor ones, and the access to them is limited. To compare the composition of both synthetic turf football pitches and playgrounds with other recycled rubber materials, 4 samples came from urban pavements (tree protectors), and 3 commercial crumb rubber tiles, one of them employed as indoor gym floor, were also considered in this study. Besides, 2 commercial crumb rubber samples were marketed, and 3 car tires were acquired in local car workshops, since car tires are, a priori the material from which the crumb rubber come from. Regarding the alternative materials, cork crumb employed as infill in a football pitch, and sand employed as paver in an outdoor playground, were also collected and analyzed.

For the crumb rubber, cork and sand, between 2 and 100 g of sample were directly collected from the studied surfaces. For the tiles and car tires, samples were cut into small particles (<3 mm). In all cases, samples were placed into a glass vial, sealed with an aluminum cap and stored at room temperature, and protected from light until their analysis took place.

2.3. Ultrasound assisted extraction (UAE)

Two hundred mg of the corresponding sample was placed in a 4 mL glass vial, and 2 mL of EtAc were added. Then, the vial was sealed with an aluminum cap furnished with PTFE-faced septum, and it was immersed into an ultrasound bath (P. Selecta, Barcelona, Spain) for 20 min, at 50 Hz and controlled temperature (25–30 °C). After extraction, the organic supernatant was filtered through 0.22 μm PTFE filters (25 mm diameter), and diluted 1:10, v/v in EtAc prior the injection in the chromatographic system. The overall process comprised a sample dilution factor of 1:100 (w/v).

2.4. GC–MS/MS analysis

Analyses were carried out employing a Thermo Scientific Trace 1310 gas chromatograph coupled to a triple quadrupole mass spectrometer (TSQ 8000) with an autosampler IL 1310 from Thermo Scientific (San Jose, CA, USA). Separation was performed on a Zebron ZB-Semivolatiles column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) obtained from Phenomenex (Torrance, CA, USA). Helium (purity 99.999%) was employed as carrier gas at a constant flow of 1.0 mL min^{-1}. The GC oven temperature was programmed from 60 °C (held 2 min) to 210 °C at 15 °C min^{-1} and to 290 °C at 5 °C min^{-1} (held 4 min). The total run time was 38 min. Pulsed splitless mode (200 kPa, held 1.2 min) was employed for injection. The injector temperature was set at 270 °C, and the injection volume was 1 μL. The mass spectrometer detector (MSD) was operated in the electron ionization (EI) positive mode (+70 eV). The temperatures of the transfer line and the ion source were set at 290 °C, and 350 °C, respectively. The filament was set at 25 μA and the multiplier voltage was 1460 V. Selected Reaction Monitoring (SRM) acquisition mode was implemented monitoring 2 or 3 transitions per compound (see Table S1) for an unequivocal identification and quantification of the target compounds. The system was operated by Xcalibur 2.2, and Trace Finder™ 3.2 software.

2.5. Chromatographic analysis

The 42 compounds determined in this work, including PAHs, plasticizers, antioxidants and vulcanizing additives are summarized in Table S1. The chromatographic conditions were optimized using a standard mixture prepared in ethyl acetate, achieving an efficient separation of most the target compounds (chromatographic conditions are described in Section 2.4).

The MS/MS working conditions were optimized using the semi-automated selected reaction monitoring (AutoSRM) tool implemented in the TSQ 8000 GC–MS/MS software. For this purpose, individual standard solutions of each compound prepared in EtAc were employed. The AutoSRM process involves three steps: (i) precursor ion study; (ii) product ion study; and (iii) SRM optimization. The experimental GC–MS/MS parameters including the retention times, the SRM transitions and CE for the studied compounds are summarized in Table S1. For some of the target compounds, the obtained MS/MS transitions were similar, but they can be successfully distinguished since they present different retention time. However, for two PAHs, B[*b*]F and B[*j*]F, both retention time and MS/MS transitions are the same. Therefore, these compounds were quantified as sum in the analyzed samples.

2.6. UAE-GC–MS/MS performance

The UAE experimental parameters, including sample size, solvent type and volume, and microwave potency were previously optimized (Celeiro et al., 2018), demonstrating that the use of 200 mg of sample, 2 mL of EtAc and 50 Hz as UAE potency, offered the highest extraction efficiency.

Under the selected conditions, the UAE-GC–MS/MS method was validated in terms of linearity, accuracy, repeatability and reproducibility. Instrumental quantification limits (IQLs), and limits of quantification (LOQs) were also calculated. The method performance parameters are summarized in Table S3. Calibration standards were prepared in ethyl acetate covering a concentration range between 0.1 and 1000 μg L^{-1} for most compounds (see specific ranges in Table S3), including 13 concentration levels and three replicates per level. The method exhibited a direct proportional relationship between the amount of each analyte and its chromatographic response, obtaining coefficients of determination (R^2) higher than 0.9906 in all cases.

Instrumental method precision was evaluated within a day ($n = 3$), and among days ($n = 6$) for all the calibration concentration levels. Relative standard deviation (RSD) values for 10 μg L^{-1} (500 μg L^{-1} for DINP, DIDP, and 2MBTZ) are also shown in **Table S3**. In all cases, the RSD values were lower than 12% and 15% for repeteability and reproducibility, respectively.

Instrumental quantification limits (IQLs) were calculated as the compound concentration giving a signal-to-noise ratio of ten ($S/N = 10$), employing standards containing low concentration of the target compounds prepared in EtAc. For two phthalates that were detected in the solvent blanks (DIBP and DEHP), IQLs were calculated as the concentration corresponding to the signal of the blanks plus ten times its standard deviation. The limits of quantification (LOQs) in the samples were estimated considering the extraction dilution process (see details in Section 2.3) by multiplying 100 times the IQL values. They are shown in Table S3, and they were at the low ng g^{-1} level for all compounds, excluding the multiple phthalates DINP and DIDP, both mixtures of branched chain isomers, and 2MTBZ, compound with a low sensitivity in GC analysis. Although samples were diluted 100 times prior analysis, as it was commented above, the method offered sufficient efficiency to ensure the analysis of these type of samples, since the limits required by the legislation are several orders of magnitude higher than those provided by the developed methodology. In any case, should more sensitivity required, the ratio of the UAE extract dilution could be lowered. However, in this case, an extract clean-up step would be necessary.

To assess the accuracy of the proposed method, recovery studies were carried out employing two different crumb rubber real samples from a synthetic turf football pitch and from an outdoor playground. The study was performed at two concentration levels 1 μg g^{-1} and 10 μg g^{-1} for all compounds, excluding 3 of the 42 compounds: the phthalate mixtures DINP and DIDP, and 2-mercaptobenzothiazole (2MBTZ) (100 μg g^{-1}). The spiked samples were extracted and analyzed by triplicate. Since some of the target compounds were found in the non-spiked real samples, the initial concentrations were taken into account to calculate the recoveries. To the best of our knowledge, this is the first recovery and accuracy study performed in this type of recycled material.

As can be seen in Table S3, good accuracy and precision were achieved, with recovery values between 72 and 116%, and RSD values lower than 15% in all cases.

3. Results and discussion

3.1. Analysis of the crumb rubber materials

Forty rubber samples from different recreational surfaces were analyzed following the UAE-GC–MS/MS procedure proposed in this study. Other rubber samples such as commercial tiles and crumb rubber, and scrap tires were also included. In addition, two green alternative materials (cork and sand) were analyzed. The description of the samples is given in Table S2.

3.1.1. Football pitches of synthetic turf

Thirteen crumb rubber samples from football pitches of synthetic turf (samples FP1-FP13, see Table S2) were analyzed. Besides, a cork sample (sample FP14), employed as infill in a football pitch was also analyzed for comparison purposes. Individual concentrations of the target compounds in the 13 analyzed samples are summarized in Table S4. Individual and total PAH contents in the synthetic turf football pitches, expressed in μg g^{-1}, are displayed in Table 1.

All samples contained PAHs, and their total concentration ranged between 8 μg g^{-1} and 95 μg g^{-1}. All the other target compounds, excluding D[*ah*]A, were found in the analyzed samples. Seven out of the 18 studied PAHs: PHEN, FLA, PYR, CHY, B[*a*]P, IND and B[*ghi*]P, were detected in all the samples, with relatively high concentrations of PYR up to 40 μg g^{-1}. The considered most potent carcinogenic PAH, B[*a*]P, was found in all samples, reaching concentrations of 3.6 μg g^{-1}. The PAH distribution per sample is depicted in Fig. S1a.

As can be seen, the profile was similar in all samples, with PYR contributing the most to the total PAH composition. This result, as well as the Σ PAHs levels agree with those reported in other studies (Celeiro et al., 2018; Diekmann et al., 2019; Han et al., 2008; Marsili et al., 2015; Schneider et al., 2020a). This includes the study of the National Dutch Institute for Public Health and the Environment (RIVM), (RIVM, 2017), where a median concentration of 5.8 μg g^{-1} for the 8 ECHA PAHs was reported, whereas in the present work, a median concentration of 6.0 μg g^{-1} was obtained for the 13 crumb rubber samples from synthetic turf football pitches.

Several authors observed a decrease of PAH concentrations in crumb rubber used for artificial turf due to ageing effects (Lioy et al., 2011; Marsili et al., 2015). However, this cannot be confirmed in the present study. The rubber granules are periodically refilled, and part of the rubber infill is dragged due to the continuous use of these sport surfaces (Celeiro et al., 2018; Han et al., 2008). Regarding the cork sample, only PHEN was found at a concentration up to two orders of magnitude lower than that found in the crumb rubber samples. The origin of this compound in the cork infill could be related with the fact that the football pitch was previously infilled with crumb rubber for a long time, and it is located in an intense traffic area. Thus, this green alternative may be a very suitable option for its use as infill in these type of sport surfaces, as regards the absence of PAH exposure for users.

Individual concentrations of the other target compounds (plasticizers, antioxidants and vulcanization agents) are summarized in Table 2. Ten out of the 19 target plasticizers were found in the 13 analyzed samples. DBP, DEHA and DEHP were detected in all the crumb rubber samples at concentrations up to 32 μg g^{-1}. The other plasticizers were detected in 2–12 samples, reaching concentration levels of 3.8 μg g^{-1}, excluding the multiple phthalate DIDP, that was detected at concentration higher than 87 μg g^{-1}. The antioxidant BHT was detected in all samples at concentrations up to 3.7 μg g^{-1}, whereas BTZ, 4TBP and 2MBTZ were found in 10, 9, and 3 samples, reaching concentrations of 34, 4 and 62 μg g^{-1}, respectively. It is worth mentioning that 2MBTZ is catalogued as a 2A group carcinogen, and as a substance of very high concern (SVHC) by ECHA, considered as a moderate skin sensitizer, and very toxic to aquatic life with long-lasting effects (ECHA, 2015). Fig. S1b exhibits the concentration of the detected plasticizers, antioxidants, and vulcanization agents in the analyzed crumb rubber samples from synthetic turf football pitches. In the cork sample, only DEP and BHT were found at low concentration (<0.3 μg g^{-1}).

3.1.2. Playgrounds

Fifteen rubber samples from both outdoor (P1-P10) and indoor (P11-P15) playgrounds have been analyzed. Besides, a sand sample, employed as playground surface (P16), was included in the study. Individual and total concentration of the PAHs and the other target compounds are displayed in Tables 1 and 2, respectively (see Table S5 for detailed results). The sand sample results were not included in the table, since none of the target compounds was detected.

Table 1
PAH concentration (μg g^{-1}) in the crumb rubber samples from synthetic turf football pitches and playgrounds.

PAHs	Football pitches of synthetic turf (FP1-FP13)				Outdoor playgrounds (P1-P10)				Indoor playgrounds (P11-P15)				Cork (FP14)
	N[a]	Range	Average	Median	N[a]	Range	Average	Median	N[a]	Range	Average	Median	Average ± RSD
NAP	12	0.04–0.90	0.3	0.1	2	0.012–0.017	0.014	0.014	3	0.03–0.09	0.05	0.04	
ACY	9	0.02–2.20	0.6	0.2	1	0.016	0.016	0.016	2	0.11–0.13	0.12	0.12	
ACE	3	0.08–0.61	0.3	0.3	1	0.012	0.011	0.011	1	0.05	0.05	0.05	
FLU	11	0.02–1.40	0.3	0.05	2	0.010–0.011	0.0105	0.0105	5	0.08–0.22	0.17	0.18	
PHEN	13	0.1–9.4	2.1	0.2	5	0.02–0.10	0.06	0.07	5	0.8–4.2	1.8	1.3	0.08 ± 0.01
ANC	10	0.01–1.60	0.4	0.1	5	0.01–0.10	0.04	0.03	4	0.07–0.88	0.3	0.2	
FLA	13	0.5–14	4.1	1.5	10	0.11–0.74	0.32	0.29	5	2.0–6.2	3.7	3.5	
PYR	13	0.8–40	12	4.3	10	0.2–2.9	1.1	1.0	5	4.9–13	8.5	6.6	
B[*a*]A	12	0.16–6.1	1.4	0.3	2	0.09–0.13	0.10	0.10	3	0.08–1.62	0.6	0.2	
CHY	13	1.4–7.5	3.2	2.6	9	0.1–1.2	0.4	0.3	5	0.4–1.3	0.7	0.6	
B[*b*]F + B[*j*]F	9	0.9–7.2	2.1	1.4	7	0.08–0.37	0.16	0.13	4	0.14–0.48	0.32	0.33	
B[*k*]F	11	0.1–2.0	0.7	0.6	2	0.06–0.8	0.42	0.42	4	0.02–0.55	0.18	0.07	
B[*e*]P	7	1.6–4.2	2.8	2.9	10	0.04–0.90	0.22	0.10	4	0.2–0.7	0.4	0.3	
B[*a*]P	13	0.4–3.6	1.1	0.9	4	0.02–0.42	0.14	0.07	3	0.05–0.16	0.10	0.11	
IND	13	0.3–1.6	0.6	0.5	4	0.05–0.14	0.08	0.07	2	0.04–0.10	0.07	0.07	
D[*ah*]A	0				0				1	0.03	0.03	0.03	
B[*ghi*]P	13	1.5–4.6	2.6	2.5	8	0.02–1.1	0.27	0.08	5	0.2–1.1	0.4	0.3	
Σ 8 ECHA PAHs	13	3–30	10	6	10	0.1–3.1	0.9	0.5	5	0.8–3.3	1.9	1.7	
Σ 16 EPA PAHs	13	8–91	32	16	10	0.9–5.6	2.5	1.7	5	9–25	17	13	0.08 ± 0.01
Σ Total PAHs	13	8–95	32	15	10	1.0–6.0	2.7	2.0	5	9–25	17	13	0.08 ± 0.01

[a] Number of samples containing the compound.

Table 2
Concentrations (μg g^{-1}) of plasticizers, antioxidants and vulcanization agents in the crumb rubber samples from synthetic turf football pitches and playgrounds.

Plasticizers	Football pitches of synthetic turf (FP1-FP13)				Outdoor playgrounds (P1-P10)				Indoor playgrounds (P11–15)				Cork (FP14)
	N[a]	Range	Average	Median	N[a]	Range	Average	Median	N[a]	Range	Average	Median	Average ± RSD
DMP	3	0.03–0.16	0.07	0.06	0				5	0.09–0.64	0.3	0.2	
DEP	9	0.04–0.70	0.2	0.1	5	0.01–1.00	0.3	0.3	5	0.5–3.3	2.0	2.1	0.04 ± 0.01
DIBP	12	0.2–3.8	1.4	1.0	7	0.1–10	1.7	0.3	5	2–84	29	16	
DBP	13	0.1–3.9	1.4	0.7	9	0.03–2.20	0.4	0.2	5	2–59	21	8	
BPA	9	0.06–1.30	0.5	0.3	5	0.05–4.50	1.4	0.6	5	0.08–4.00	1.7	2.1	0.27 ± 0.03
BBP	3	0.3–1.7	0.6	0.3	3	0.03–0.09	0.05	0.04	5	0.4–2.6	1.3	1.2	
DEHA	13	0.1–32	5.8	1.8	7	0.02–0.20	0.1	0.2	5	6.4–48	25	16	
DIHP	2	2.1–2.5	2.3	2.3	1	0.15	0.15	0.15	3	0.8–3.7	2.0	1.7	
DEHP	13	0.9–28	9.2	8.0	9	0.5–4.0	1.6	1.2	5	9–46	30	38	
DnOP	0				0				2	38–76	57	57	
DINP	0				2	84–92	88	88	3	34–2105	870	471	
DIDP	2	87–180	133	133	3	10–89	49	49	4	11–7331	1882	94	
Antioxidants and vulcanization agents													
BHT	13	0.06–3.70	1.1	1.0	6	0.01–0.30	0.1	0.1	5	0.2–0.9	0.5	0.6	0.18 ± 0.07
BTZ	10	0.6–34	9.1	2.7	2	0.6–0.8	0.7	0.7	4	1.8–15	12	15	
4TBP	9	0.05–4.10	1.8	1.3	3	0.03–0.51	0.3	0.3	5	0.2–1.2	0.6	0.6	
2MBTZ	3	29–62	43	39	0				1	190	190	190	

[a] Number of samples containing the compound.

All outdoor and indoor playground samples contained PAHs, being their total concentration between 1.0–6.0 μg g^{-1} and 9–25 μg g^{-1}, respectively. Three out of the 18 targeted, FLA, PYR and B[*e*]P, were found in all the analyzed outdoor samples at concentrations up to 2.9 μg g^{-1}, whereas in the indoor analyzed samples, 6 of them, PHEN, ANC, FLA, PYR, CHY, and B[*ghi*]P, were detected in all the samples, reaching concentrations up to 13 μg g^{-1}. The other PAHs were found in 10–80% of the analyzed samples, excluding D[*ah*]A that was only found in one indoor sample. The total PAH concentration was lower than those reported in studies performed several years ago (Diekmann et al., 2019; Lioy et al., 2011; Llompart et al., 2013). This can be attributed to the fact that the REACH regulation aimed at eliminating the use of so-called 'PAH-rich' extender oils in tires produced after January 2010 (Off J Eur Union, 2015). This is resulting in an obvious reduction of PAH in crumb rubber, and a further decrease is expected since the called 'carbon black', used as a reinforcing filler (up to 30% of every tire), was listed as a carcinogen by the International Agency for Research on Cancer (IARC). However, this PAH concentration decrease was not observed in the crumb rubber employed as infill in synthetic turf football pitches, as it was in a previous study reported by the authors (Celeiro et al., 2018). This might suggest that the rubber material used for the construction of synthetic turf football pitches and playgrounds could come from different origins. Several authors observed that crumb rubber from non-EU tires, for which the REACH regulation (commented above) is not applicable (Off J Eur Union, 2015), contained more PAHs than those from EU origin. In addition, these studies suggest that not only car tires are employed to obtain crumb rubber, other elastomeric materials like gaskets or brake tubes can be recycled as well, and used as infill in synthetic turf football pitches, increasing the PAH content (Fornai, 2016, Diekmann et al., 2019). Nowadays, there are no regulations governing the declaration of the origin of rubber (previous use, country, age…) (Diekmann et al., 2019).

The PAH distribution profile for the analyzed playground samples is depicted in Fig. S2a. A comparison between the mean PAH concentrations in crumb rubber from synthetic turf football pitches and playgrounds can be seen in Fig. 1a. The profile for playgrounds is slightly different from that obtained for the crumb rubber samples collected in football pitches of synthetic turf. In this last case, PYR and FLA were the most important contributors to the total PAH content, with a difference up to two of magnitude order compared to the other detected PAHs. This behavior was also observed in the indoor playground samples. As regards the outdoor playgrounds, the PAH with the highest contribution to the total concentration was also PYR, followed in this case by CHY. As regards the PAH profiles, PYR, FLA and PHEN concentrations were up to 2 orders of magnitude higher in indoor playgrounds, than in outdoor playgrounds. However, in any case, the average PAH concentrations were clearly lower in both types of playgrounds in comparison with those obtained in the football pitches.

Regarding plasticizers, 12 out of the 19 studied compounds were detected in the indoor samples and 10 of them in the outdoor playgrounds as it is depicted in Fig. S2b. The presence of the endocrine disruptor BPA, at concentration levels up to 4 μg g^{-1}, in 50% of the outdoor playgrounds and in all the indoor playgrounds should be underlined. The presence of DEHP in most samples, at concentration up to 46 μg g^{-1}, is also notable. However, these values, as well as those obtained for other phthalates such as DBP and DIBP are up to two orders of magnitude lower than the reported in indoor playgrounds and commercial pavers (Celeiro et al., 2014; Llompart et al., 2013) manufactured prior the entry into force of the last phthalate restriction in plasticized materials (2018b). The higher phthalate concentration, especially those of DINP and DIDP (concentrations levels of thousands of μg g^{-1} in an indoor shopping center playground), and the fact that the crumb rubber material is more compacted in the indoor facilities than in the outdoor ones, might suggest that other plastic materials or other components such as glues and adhesives could have been used to bind the material and to fix it on different surfaces.

BHT, BTZ and 4TBP were found in all the indoor samples and in several outdoor playground samples, at concentrations reaching 15 μg g^{-1}, whereas 2MBTZ was found at 190 μg g^{-1} in only one indoor sample. The indoor samples were collected from shopping centers and airports, both very crowded places, where the main users of these surfaces are children and where hand-to-mouth contact is very frequent, favoring the entrance of the hazardous chemicals into the organism, together with the other routes (dermal and respiratory).

As regards the sand sample, although it was collected from a playground located within an intense traffic area, none of the target compounds was detected. Some authors relate the PAH content of this kind of recreational rubber surfaces with the emissions coming from urban traffic areas (Tarafdar et al., 2019). However, in this case, a porous material such as a sand surface appeared completely clear of contaminants, demonstrating its suitability as environmentally friendly and safe material to be used in playgrounds.

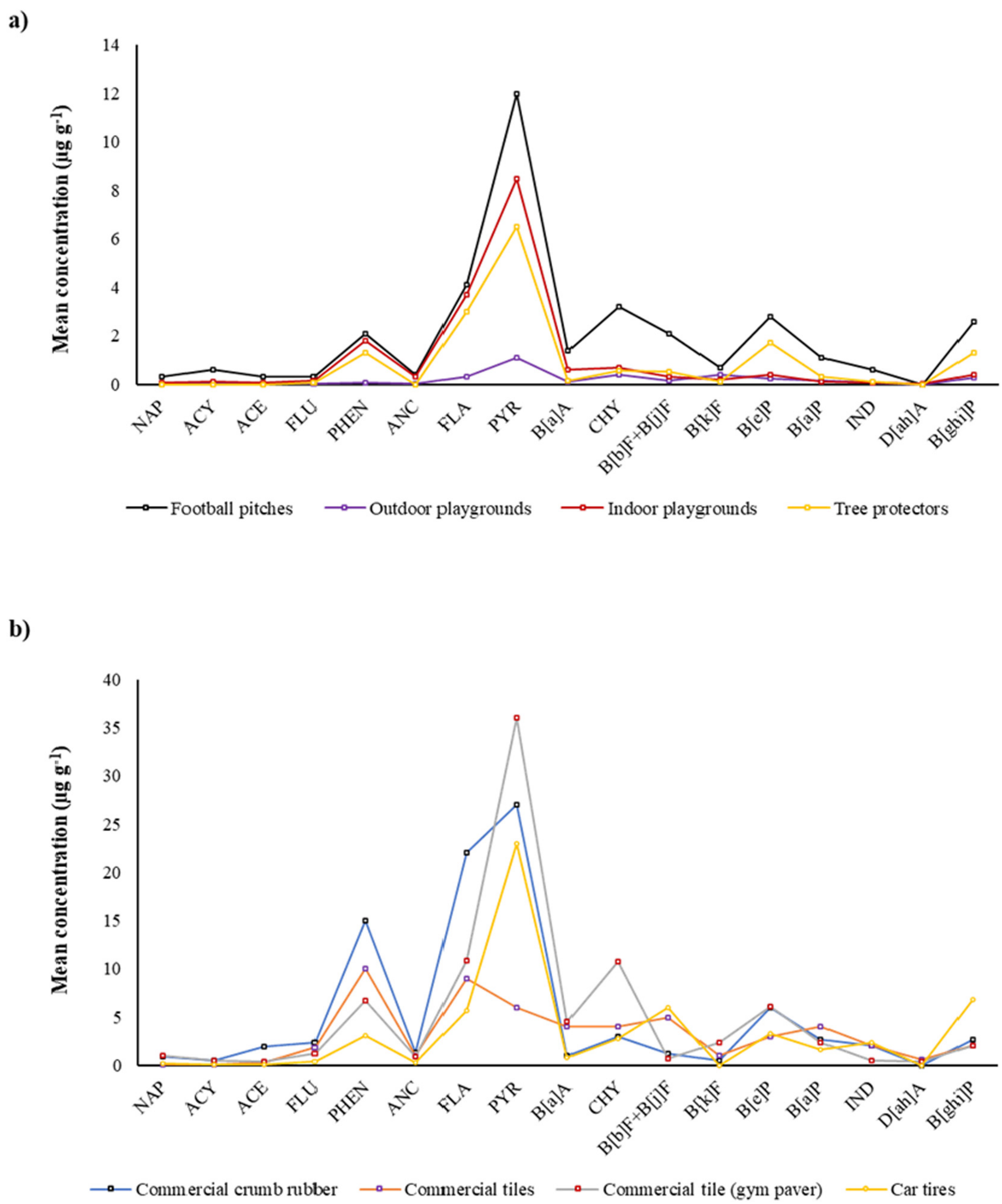

Fig. 1. Mean PAH concentrations obtained in a) football pitches, playgrounds and tree protectors and b) commercial crumb rubber, commercial tiles (values divided by 100), gym paver and car tires.

3.1.3. Urban surfaces, commercial tiles and crumb rubber, and scrap tires

Other crumb rubber samples from different origin were analyzed, including 4 urban surfaces employed as tree protectors (U1-U4), 3 commercial tiles (T1 and T2 were bought in the same local market, whereas T3 was on-line marketed, and it is currently being used as an indoor gym floor), and 2 commercial rubber granulates (R1, R2). Besides, 3 used car tires were analyzed (samples C1-C3). Detailed quantification results are shown in Table S6. Tables 3 and 4 summarize the total PAH and other target compound compositions, respectively.

3.1.3.1. Tree protectors. Thirteen target PAHs were detected in the four analyzed rubber tree protectors, reaching a total concentration of 18 µg g^{-1}. These urban surfaces, as well as the outdoor playgrounds and football pitches, are exposed to meteorological conditions (rain, temperature changes…) and, probably for this reason, the presence of the most volatile PAHs (NAP, ACY, ACE) was not detected, as it is shown in Fig. 1a. However, for the other PAHs, the profile for these urban pavements is similar than that observed indoor playgrounds.

Nine out of the 19 target plasticizers were found, highlighting the presence of the multiple phthalates DINP and DIDP, at hundreds and thousands of µg g^{-1} in several samples. BHT was found in two of the four analyzed samples, whereas BTZ and 4TBP were detected in all samples, reaching concentration of 18 µg g^{-1}.

3.1.3.2. Commercial rubber tiles. As can be seen in Table 3, all target PAHs were found in the three analyzed commercial rubber crumb tile samples (T1-T3), highlighting the extremely high concentrations reached by PHEN and FLA, close to 1000 µg g^{-1} in samples T1 and T2. Concentrations detected in sample T3, a pavement tile employed in an indoor

Table 3
PAH concentration (μg g^{-1}) in the crumb rubber samples from urban pavements (tree protectors), commercial rubber tiles and granulates, and car tires.

PAHs	Tree protectors (U1-U4)				Commercial products							Car tires (C1-C3)			
					Tiles (T1-T2)			Gym paver (T3)	Rubber granulates (R1-R2)						
	N[a]	Range	Average	Median	N[a]	Range	Median	Average ± RSD	N[a]	Range	Median	N[a]	Range	Average	Median
NAP	0				2	4–6	5	1.15 ± 0.03	2	0.3–1.6	0.9	2	0.15–0.19	0.17	0.17
ACY	0				2	11–14	12	0.5 ± 0.1	2	0.4–0.8	0.5	3	0.07–0.12	0.10	0.11
ACE	0				2	27–31	29	0.4 ± 0.1	2	0.1–3.6	1.9	2	0.12–0.13	0.13	0.13
FLU	1	0.09	0.09	0.09	2	184–193	188	1.2 ± 0.3	2	0.4–4.4	2.4	3	0.1–0.5	0.4	0.5
PHEN	2	0.7–2.1	1.3	1.3	2	1043–1072	1057	6.7 ± 0.3	2	3.7–28	15	3	1.6–6.2	3.1	1.7
ANC	0				2	232–257	244	0.88 ± 0.05	2	0.6–2.1	1.3	3	0.1–0.5	0.3	0.4
FLA	2	2.1–3.9	3.0	3.0	2	928–997	962	10.9 ± 0.2	2	10–34	22	3	2.3–10	5.7	3.9
PYR	4	1–10	6.5	7.4	2	681–701	691	36 ± 2	2	24–31	27	3	12–40	23	16
B[*a*]A	4	0.1–0.2	0.15	0.14	2	405–484	444	4.5 ± 0.2	2	0.4–1.7	1.0	1	0.8	0.8	0.8
CHY	4	0.4–0.7	0.57	0.59	2	440–504	472	10.8 ± 0.3	2	1.2–4.8	3.0	3	0.3–7.9	2.8	0.3
B[*b*]F + B[*j*]F	4	0.2–1.0	0.52	0.39	2	442–562	502	0.68 ± 0.04	2	2.4–3.9	1.2	1	6.0	6.0	
B[*k*]F	3	0.04–0.17	0.13	0.13	2	110–155	132	2.4 ± 0.7	2	0.4–0.6	0.5	0			
B[*e*]P	4	0.3–5.0	1.7	0.7	2	273–350	311	6.1 ± 0.1	2	5–7	6.0	3	0.4–8.3	3.3	0.5
B[*a*]P	2	0.07–0.52	0.3	0.3	2	372–492	432	2.4 ± 0.6	2	0.4–5.4	2.7	2	0.2–2.9	1.6	1.6
IND	2	0.07–0.19	0.1	0.1	2	173–252	212	0.5 ± 0.1	2	0.2–3.8	2.0	1	2.4	2.4	2.4
D[*ah*]A	0				2	55–72	63	0.4 ± 0.1	0			0			
B[*ghi*]P	4	0.3–3.1	1.3	1.0	2	168–264	216	2.1 ± 0.3	2	1–4	2.7	2	1.2–12	6.8	6.8
Σ 8 ECHA PAHs	4	1–7	3.2	2.5	2	2097–2619	2353	26	2	15–16	16	3	1–27	9.5	1.1
Σ 16 EPA PAHs	4	5–17	12	12	2	5117–5712	5665	82	2	51–123	87	3	18–92	45	24
Σ Total PAHs	4	6–18	13	15	2	5611–6343	5977	88	2	56–130	93	3	18–100	48	24

[a] Number of samples containing the compound.

gym flooring, were high but, in general, two orders of magnitude lower than in the other two samples. In this sample, the important contribution of PYR, FLA and CHY (sum, 57 μg g^{-1}) to the total PAH concentration (88 μg g^{-1}), must be highlighted. For samples T1 and T2, the total PAH content was higher than 5600 μg g^{-1}. In these tile samples, 8 plasticizers were also detected, including DEHP at concentrations up to 95 μg g^{-1}. The multiple phthalates DINP and DIDP were also found at concentrations of 153 μg g^{-1}. The other target compounds, BHT, BTZ and TBP were found in two samples, reaching concentrations of 7.2 μg g^{-1}. In general, the concentration range of plasticizers, antioxidants and vulcanization agents was similar to that observed in the indoor playgrounds.

3.1.3.3. Commercial crumb rubber. Two commercial crumb rubber samples were analyzed (R1-R2). 16 out of the 18 target PAHs were found, reaching a total concentration of 130 μg g^{-1}. The PAHs showing the highest concentration were PYR and FLA, being their contribution about 30% of the total PAH content. These results agree with those reported on the total PAH content of recycled crumb rubber from European recyclers companies (Schneider et al., 2020b).

Although the PAH profiles of these samples are similar to those obtained in football pitches (see Fig. 1a and b), the mean concentrations are clearly higher. Although only two commercial crumb rubber samples were analyzed in this study, these results are in concordance with those reported by Schneider et al. (2020a), who analyzed different crumb rubber samples obtained directly from recyclers companies. The mean concentration of PYR was 25 μg g^{-1}, similar to those found in the commercial crumb rubber samples included in this study (27 μg g^{-1}), and clearly higher than those measured in the crumb rubber employed as infill in synthetic turf football pitches of this study (12 μg g^{-1}).

Table 4
Concentrations (μg g^{-1}) of plasticizers, antioxidants and vulcanization agents in the crumb rubber samples from urban pavements (tree protectors), commercial rubber tiles and granulates, and car tires.

Plasticizers	Tree protectors (U1-U4)				Commercial products							Car tires (C1-C3)			
					Tiles (T1-T2)			Gym paver (T3)	Rubber granulates (R1-R2)						
	N[a]	Range	Average	Median	N[a]	Range	Median	Average ± RSD	N[a]	Range	Median	N[a]	Range	Average	Median
DMP	0				0				2	0.03–0.09	0.06	0			
DEP	1	0.14	0.14	0.14	2	0.7–0.9	0.8	0.18 ± 0.04	2	0.06–0.24	0.15	3	0.4–0.9	0.6	0.5
DIBP	4	0.1–0.8	0.4	0.5	2	3.0–4.3	3.6	3.7 ± 0.2	2	1.2–2.1	1.6	3	2–19	12	15
DBP	4	0.1–1.5	0.5	0.3	2	4.1–4.8	4.4	4.5 ± 0.6	2	0.4–1.8	1.1	3	2–7	5	4
BPA	2	0.3–0.5	0.4	0.4	0				2	0.2–3.2	1.7	3	0.7–17	6.2	1.8
BBP	2	0.07–0.17	0.12	0.12	2	0.1–0.3	0.2	0.13 ± 0.02	2	0.1–0.4	0.2	3	0.4–1.8	0.9	0.4
DEHA	2	0.1–0.2	0.17	0.17	2	7.8–7.9	7.85	54 ± 8	2	1–9	5	3	10–56	27	14
DIHP	0				0				2	0.8–2.2	1.5	0			
DCHP	0				0				0			3	2–3	2.6	2.9
DEHP	4	0.9–5.1	2.6	2.2	2	62–95	78	12 ± 3	2	1–10	5	3	1–91	42	18
DINP	2	165–193	179	179	2	100–107	104	38 ± 3	0			0			
DIDP	2	440–1153	796	796	2	141–153	147	156 ± 35	0			0			
Antioxidants and vulcanization agents															
BHT	2	0.04–1.40	0.72	0.72	1	7.2	7.2	0.40 ± 0.02	2	0.6–1.4	1.0	3	0.2–0.4	0.3	0.3
BTZ	4	1.1–18	8.2	6.9	1	1.5	1.5	1.39 ± 0.04	2	6–20	13	3	13–70	46	56
4TBP	4	0.05–0.31	0.1	0.08	1	4.5	4.5	0.4 ± 0.1	2	3.0–3.9	3.4	3	0.2–0.7	0.5	0.7

[a] Number of samples containing the compound.

Regarding plasticizers, nine were found at concentration up to 10 μg g^{-1}. Besides, the antioxidant BHT and the vulcanization agents BTZ and 4TBP were detected in the two crumb rubber samples, reaching concentrations of 20 μg g^{-1}.

3.1.3.4. Car tires. The analysis of three car tire samples (C1-C3) were included in the present work. The target compound concentrations are summarized in Table 4. Fifteen out of the 18 target PAHs were detected, with PYR showing the highest concentration in the three samples with values up to 40 μg g^{-1}. The total PAH concentration were 100 μg g^{-1}, similar to those obtained for the commercial crumb rubber samples, but much lower than those found in two of the commercial tiles that came from the same supplier. Regarding the mean PAH concentrations, as shown in Fig. 1b, these two commercial tiles exhibit a completely different profile compared with the commercial rubber granulates and car tires.

Eight plasticizers (DEP, DIBP, DBP, BPA, BBP, DEHA, DCHP and DEHP) were found in all samples, reaching concentration values of 91 μg g^{-1} for DEHP. The antioxidant BHT and the vulcanizing agents BTZ and 4TBP were also found in the three car tires, at low concentration (<1 μg g^{-1}), excluding BTZ (13–70 μg g^{-1}).

3.2. Applicable legislation and future perspectives

Until now, the crumb rubber material employed as infill in synthetic turf football pitches or children playgrounds and other recreational surfaces, has been considered as a mixture supplied to the general population. Therefore, the individual concentration limits for PAHs were set at 100 μg g^{-1} for B[*a*]P and D[*ah*]A, and at 1000 μg g^{-1} for other six PAHs (B[*e*]P, B[*a*]A, CHY, B[*b*]F, B[*j*]F and B[*k*]F) (2018a). These maximum levels are disproportionately high, considering the intense use of these facilities, and taking into account the restricted levels for the eight ECHA PAHs in rubber consumer products that come into direct contact with the skin or the oral cavity (1 μg g^{-1}) or in toys (0.5 μg g^{-1}) (JRC, 2018).

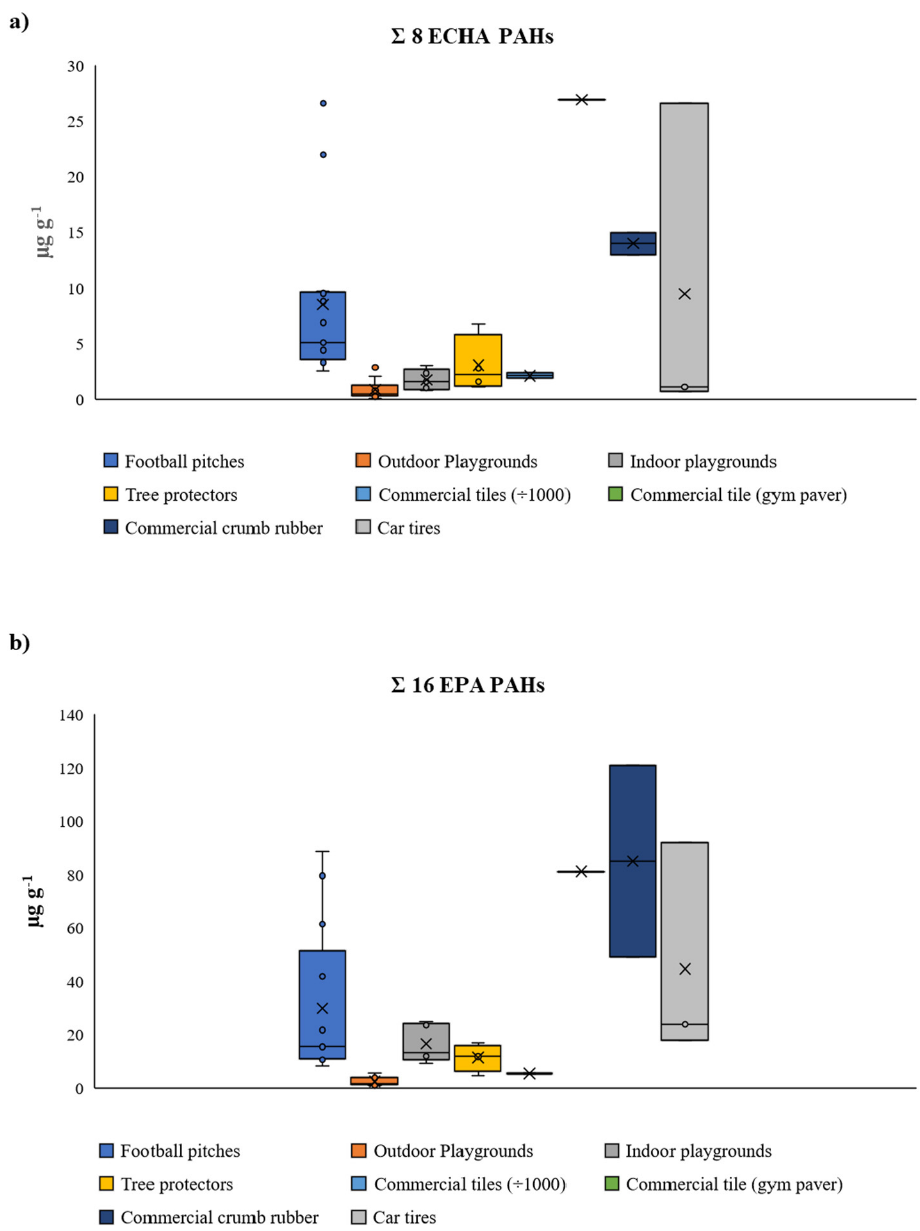

Fig. 2. Box-and-Whisker charts for a) Σ8 ECHA PAHs and b) Σ16 EPA PAHs in the different analyzed recycled rubber samples. (Values divided by 1000 for the commercial tiles).

The users of the recycled rubber recreational surfaces are mainly children that have a frequent and direct contact with the crumb rubber material. Since PAHs are recognized carcinogenic compounds, the European Commission has recently (September 2019) limited the total concentration of the 8 ECHA PAHs to 20 μg g^{-1} in granules and mulches used in synthetic turf pitches and playgrounds (ECHA, 2019).

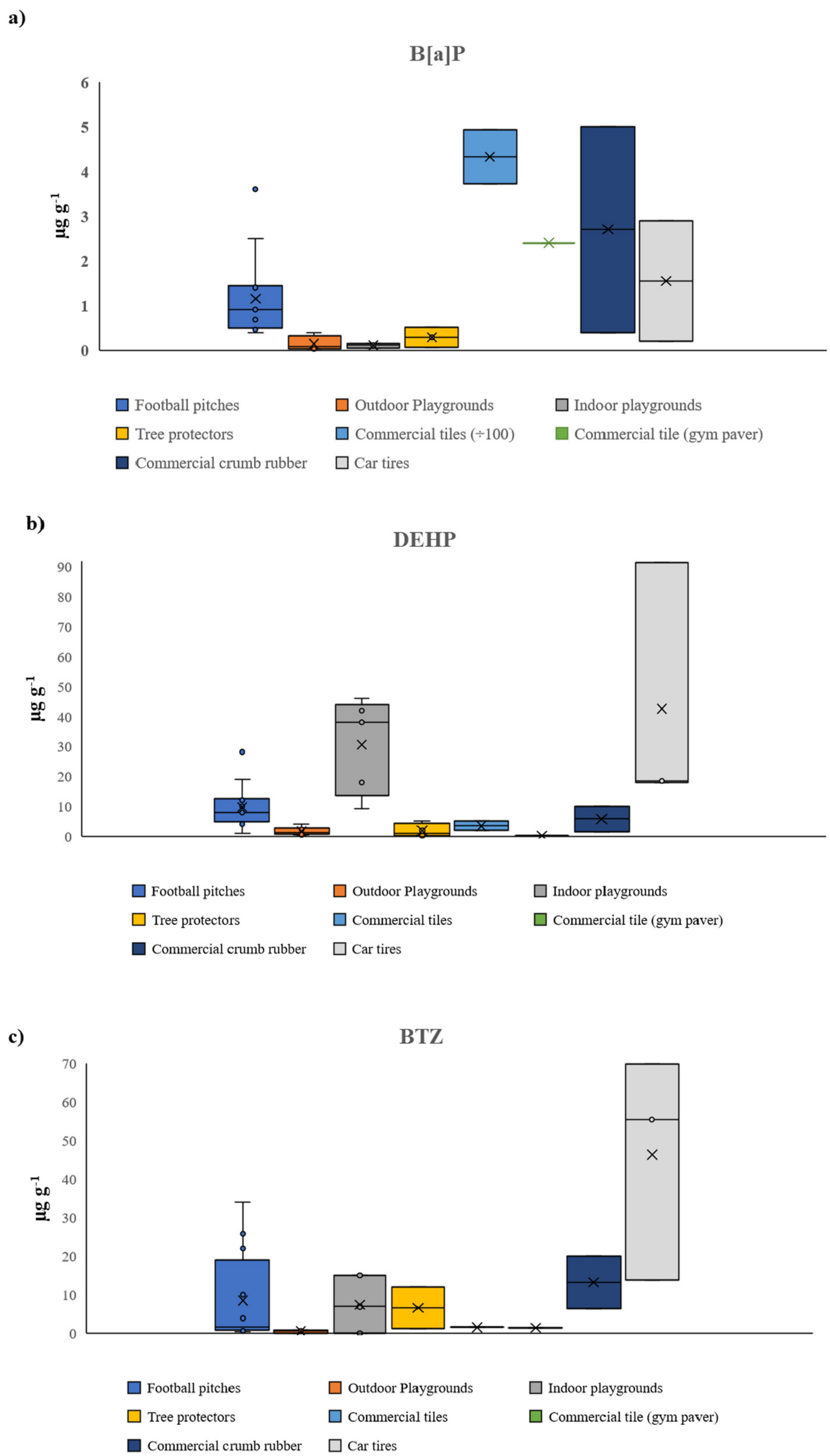

Fig. 3. Box-and-Whisker charts for some representative compounds a) B[*a*]P (values divided by 100 for the commercial tiles), b) DEHP and c) BTZ in the different analyzed recycled rubber samples.

This final opinion was adopted supporting the proposal of RIVM that suggested a combined concentration limit of 17 μg g^{-1} to address the risks from the eight ECHA PAHs (ECHA, 2018). It is expected that in next months the final decision will be forwarded to the European Commission. If considered appropriate, a draft restriction action will be prepared to amend the REACH Restrictions list (Annex XVII).

In addition, the ECHA is also progressing with its proposal to restrict the addition of microplastics to reduce the potential environmental risks. The granular infill material used in artificial turf pitches is understood to be an 'intentionally-added microplastic'. A public consultation on this proposal has been recently conducted to obtain the opinion of the RAC and SEAC, prior reaching a final decision and setting future restriction (ECHA, 2019).

To easily compare the PAH contents in the crumb rubber samples coming from the different analyzed surfaces, Fig. 2a shows the Box-and-Whisker charts, which include the average, median and concentration range for the sum of eight ECHA and 16 EPA PAHs. As can be seen, the different recreational surfaces included in this study meet the recently proposed legal limit of 20 μg g^{-1} for the eight ECHA PAHs. Only two of the analyzed commercial tiles, both obtained from the same distributor, do not comply with this requirement. It is hard to explain the high PAH concentration found in these two products, since car tires show considerably lower PAH levels. It is possible that the crumb rubber come from a different origin or/and include additional components than those typically employed in car tires. Although most of the other recycled rubber surfaces studied comply with the limit of 20 μg g^{-1} for the eight ECHA PAHs, this may be still a concern for children as they are the main users of these facilities. As such, the dermal absorption, inhalation and even ingestion of the crumb rubber suggest a likely high exposure. Therefore, further studies should be conducted to evaluate whether the proposed restriction is the most appropriate action to control the risks posed by the substances studied. Maybe this restriction should be tightened to be in concordance with the established maximum level in rubber consumer products (1 μg g^{-1}) or even in toys (0.5 μg g^{-1}) for the eight PAHs considered as carcinogenic by the ECHA (JRC, 2018).

Fig. 3 shows Box-and-Whisker plots for three representative hazardous compounds in the various analyzed samples. B[*a*]P, which distribution is depicted in Fig. 3a, was selected since it is the most potent carcinogenic compound among the PAHs, and its concentration is a good indicator of the total carcinogenic potency of a PAH mixture (Hernández et al., 2019). In addition, since it is one of the eight ECHA PAHs, its maximum concentration in rubber consumer products is set to 1 μg g^{-1}, or 0.5 μg g^{-1} in toys. As can be seen, most of the studied surfaces meet the limit of 20 μg g^{-1}, excluding again the two marketed tile samples supplied by the same distributor, with a concentration that clearly exceeds the limit set for rubber consumer products. Fig. 3b shows the Box-and-Whisker plot for DEHP. This compound is considered as an endocrine disruptor and its presence is restricted in toys, childcare products and plasticized material (2018b). As can be seen, car tires showed the highest DEHP concentrations, with values ranging from 18 to 91.5 μg g^{-1}. The active vulcanization agent BTZ may volatilize from crumb rubber and may provoke exposure by inhalation. In general, the highest concentration levels were also observed in the car tires followed by football pitches, indoor playgrounds, and tree protectors, as can be seen in Fig. 3c.

4. Conclusions

Forty crumb rubber samples coming from different sport, recreational and urban surfaces were analyzed by UAE-GC–MS/MS. Forty-two hazardous organic compounds such as PAHs, phthalates, adipates, antioxidants, and vulcanization agents were targeted. The results revealed the presence of 30 out of these 42 target compounds in the crumb rubber samples collected in synthetic turf football pitches and playgrounds, the Σ16 EPA PAHs ranging from 8 to 91 μg g^{-1}, and from 0.9 to 25 μg g^{-1}, respectively. The mean PAH concentrations were lower in the outdoor playgrounds than in the indoor ones, and in any case, the concentrations in the two types of playgrounds were lower than those found in the football pitch samples. In general, the different crumb rubber recreational surfaces included in this study meet the recent proposed legal limit of 20 μg g^{-1} for the eight ECHA PAHs, excluding two of the analyzed commercial tiles coming from the same supplier that clearly exceed the legal limits. Further studies should be conducted to evaluate whether the proposed restriction is the most appropriate action to control the risks posed by these substances, especially for children. We suggest the present restriction should be tightened to be in line with the maximum levels established in rubber consumer products intended to be in contact with skin, or in toys.

The analysis of alternative materials such as cork revealed the absence of PAHs and other compounds, thus offering a safe and sustainable alternative to crumb rubber for the manufacture of recreational or sport facilities.

CRediT authorship contribution statement

Maria Celeiro: Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Daniel Armada:** Formal analysis, Investigation, Data curation. **Thierry Dagnac:** Conceptualization, Writing - review & editing. **Jacob de Boer:** Conceptualization, Writing - review & editing. **Maria Llompart:** Conceptualization, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.142566.

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